A FUNDAMENTAL THEORY OF SUPERCONDUCTIVITY

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Although phenomenological theories of superconductivity are now well developed, there is still need for an adequate fundamental theory based directly on the quantum behavior of the electrons and the lattice. Recently Schafroth[1] has shown that a Bose gas of charged particles would show the Meissner effect. Also, Bardeen[2] has shown that a separate particle system where all excited electronic levels are separated from the "surface of the Fermi sea" by a finite energy will show the Meissner effect.

Our analysis of the problem will be mo e descriptive than mathematical and will be similar in many respects to the theory of liquid helium II.[3]

The key feature is the finite binding energy of electron pairs or, more precisely, the finite energy required to excite the electronic system in modes other than translational flow of the entire system.

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Our general knowledge of chemical substances leads us to expect electron pairing. In molecules chemical bonding is strongest for completely paired electrons in all but the rarest cases (such as O_2). We normally find unpaired electrons associated only with atomic inner shells, which are not involved in bonding such as in the rare earths. Metals at room temperature are indeed an exception to this general situation (although the fraction of unpaired electrons is infinitesimal). Simple theories of metals which are successful in many other respects fail to predict superconductivity; however, these theories fail to take adequate account of coulombic repulsion of electrons and make the assumption of a perfect lattice of stationary nuclei.

It is known[4] that lattice distortions tend to produce breaks in the energy-level bands. If a single distortion lowers the electronic energy sufficiently (more than the energy of zero-point vibration in the corresponding mode), then permanent distortion occurs. Even for a lattice which is perfect in the mean location of the atoms, however, the total energy must be averaged over the various distortions which arise from zero-point vibration. Thus, while the electronic state with com-

plete pairing of spins may be stable by only an infinitesimal margin for a perfect lattice, this margin may be expected to become finite when averaged over the distortions of the lattice.

Let us also discuss this question in terms of Pauling's[5] theory of metallic binding. One notes that there are a number of locations in the lattice that are appropriate for chemical bonds, i.e., the shortest distances occurring between atoms. In a metal the number of these bond sites exceeds the number of bonding electron pairs. This is in contrast to a crystal such as diamond where the number of sites is precisely equal to the number of bonding electron pairs.

In addition to the bond sites, one must consider the available atomic orbitals suitable for bonding electrons. While almost always a pair of suitable orbitals can be found for each bond site, there are limitations on the number and arrangement of orbitals which may be occupied simultaneously. Thus in graphite, while the 2p orbital perpendicular to the plane is appropriate for the formation of a π bond in any one of the three bond sites adjacent to the atom, only one of these bonds can be formed at a given time. This limitation is important and, while less restrictive in true metals, must be kept in mind. It will be more restrictive in metals where the ratio of electrons to valence-shell orbitals is high. Many such metals show superconductivity, while those with a low ratio of electrons to orbitals do not.

Pauling now constructs wave functions in which the electrons occupy these bond sites and bond orbitals either in pairs or singly. Coulombic repulsion between electrons is very strong; consequently the set of sites occupied in a low-energy wave function must maintain uniform charge density. The true wave function is taken as the optimum linear combination of these component functions (in the manner of quantum-mechanical resonance). The lowest energy is obtained if the electrons, which occupy orbitals singly in one component function, have spins paired, because the resonance may then include other functions with these electrons in a single bond orbital.

Such a system of electrons is free to move collectively through the lattice and thus conduct electricity. Symbolically one may write a possible wave function for a flowing metallic electronic system:

$$\Psi = \Phi \exp i\boldsymbol{k} \cdot (\sum_i \boldsymbol{R}_i), \qquad (1)$$

where Φ is the wave function of the system in the absence of flow and the $\boldsymbol{R}_i$ vectors locate the electrons. Feynman[3] discusses this type of function more fully in connection with He II. The question of resistance, i.e., energy loss, from such a flow will be considered later.

Now let us recognize that the lattice is vibrating with zero-point amplitude supplemented by any lattice thermal excitation. As the lattice oscillates, some bond sites will become of more nearly ideal length than others. Also, the angles change, and it will be more favorable in terms of atomic orbitals to occupy certain sets of bond sites than others. The electrons will tend at all times to occupy the more favorable bond sites for a large fraction of the time.

We now consider the change when one electron spin is reoriented so that there are two more spins of one sign than of the other. These two electrons now require separate orbitals at all times, whereas before they could occupy a single orbital.